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(54) Process for preparation of polyphenylene-sulfide resins.

(52) Disclosed is a process for the preparation of polyphenylene-sulfide resins, wherein an aromatic polyhalide compound is reacted with an alkali metal sulfide, or hydrogen sulfide and an alkali metal base, or an alkali metal hydrosulfide and an alkali metal base in the presence of an amide polar solvent. A polyphenylene-sulfide resin having a cyclic oligomer content lower than 15% by weight, as determined according to the methylene chloride extraction method, is obtained by (a) carrying out the reaction in the absence of a polymerization aid, (b) using the amide polar solvent in an amount not larger than 400 g per mole of the aromatic polyhalide compound, and (c) subjecting the polymerization liquid obtained by the reaction to hot solid-liquid separation at a temperature of at least 50°C but below the boiling point of the solvent used, and washing the separated solid with the solvent used for the reaction, which is heated at a temperature of at least 50°C but below its boiling point.

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# PROCESS FOR PREPARATION OF POLYPHENYLENE-SULFIDE RESINS

The present invention relates to an improved process for the preparation of polyphenylene-sulfide resins, in which low-molecular-weight by-products formed in preparing a polyphenylene-sulfide resin are effectively removed and a polyphenylene-sulfide resin is obtained which is characterized in that generation of a gas is controlled when the resin is mixed with glass fibers or an inorganic filler and kneaded by an extruder and further in that molded bodies having highly improved mechanical strength can be formed from the resin.

Polyphenylene-sulfide resins have heretofore been used mainly as resins for injection molding, but these resins have the drawback that when the resin alone is used as a molding material, the resulting molded article has insufficient mechanical strength, especially impact strength. Accordingly, the polyphenylene-sulfide resin is generally used after having been reinforced with a reinforcer such as glass fiber or carbon fiber. Furthermore, an inorganic filler such as talc or calcium carbonate is generally incorporated in the polyphenylenesulfide resin. An extruder heated at about 300°C is ordinarily used for kneading the polyphenylene-sulfide resin with such a fibrous reinforcer or filler. However, if kneading is carried out at such a high temperature, a gas having an extremely unpleasant smell is generated at the vent of the extruder, and therefore, the environment is often adversely affected. Even in the case of a polyphenylene-sulfide resin reinforced with the above-mentioned reinforcer, the impact strength is still not sufficient and improvement is desired. Particularly, in the case of a thin molded article, improvement of the impact strength is eagerly desired. The improvement of the mechanical strength, especially the impact strength, of polyphenylene-sulfide is ordinarily accomplished by increasing the polymerization degree of polyphenylene-sulfide. To increase the polymerization degree of polyphenylene-sulfide, it is necessary that the reaction is carried out in the presence of an expensive polymerization aid such as a lithium halide, an alkali metal carboxylate or an alkali metal sulfonate, as disclosed in JP-A-59-115331. The polymerization aid is used in such a large amount as 0.5 to 1.0 mole per mole of the aromatic polyhalide compound, and it is necessary to separate the polymerization aid present in a large amount from the obtained polymer and perform a regeneration treatment. Therefore, this technique is not advantageous from the economical viewpoint.

A process for preparing polyphenylenesulfide without using a polymerization aid is also known (see, for example, JP-B-45-3,368).

It has now been found that cyclic low-molecular-weight polymers and non-cyclic low-molecular-weight polymers are contained in the polyphenylene-sulfide resin obtained according to this process and if the content of the cyclic low-molecular-weight polymers is not controlled to a level lower than a specific value, gas generation cannot be controlled satisfactorily and the mechanical strength, especially the impact strength, cannot be substantially improved.

It is the primary object of the present invention to provide a process for preparing, without using a polymerization aid as described above, a polyphenylene-sulfide having a high degree of polymerization and improved mechanical strength, especially impact strength which does not generate an unpleasant smell at high-temperature treatment.

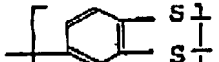
In accordance with the present invention, there is provided a process for the preparation of polyphenylene-sulfide resins, which comprises reacting an aromatic polyhalide compound with an alkali metal sulfide, or hydrogen sulfide and an alkali metal base, or an alkali metal hydrosulfide and an alkali metal base in the presence of an amide polar solvent to form a polyphenylene-sulfide resin, characterized in that (a) the reaction is carried out in the absence of a polymerization aid, (b) the amide polar solvent is used in an amount not larger than 400 g per mole of the aromatic polyhalide compound, and (c) the polymerization liquid obtained by completion of the reaction is subjected to hot solid-liquid separation at a temperature of at least 50°C but below the boiling point of the solvent used, and the separated solids are washed with the solvent used for the reaction, which is heated to a temperature of at least 50°C but below the boiling point, to remove the mother liquid adhering to the solids, whereby a polyphenylene-sulfide resin is obtained which has a cyclic oligomer content lower than 1.5% by weight, as determined according to the methylene chloride extraction method.

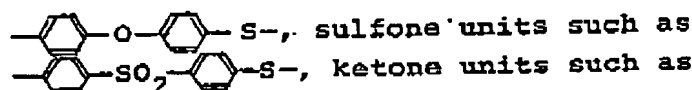
A polymer comprising at least 90 mole% of recurring units represented by the formula



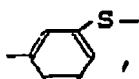
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is preferred as the polyphenylene-sulfide having a high polymerization degree, obtained according to the process of the present invention. If the content of these recurring units is less than 90 mole%, the crystallinity and heat resistance of the polymer degrade. Generally, the polymer may contain other copolycondensation units, so long as the content is up to 10 mole%. Such copolycondensation units may be trifunctional

units such as , ether units such as



meta-bonding units such as



sulfide bonds containing a phenyl nucleus having an alkyl or aryl substituent and aliphatic sulfide bonds.

The polyphenylene-sulfide consisting of the above-mentioned structural units is synthesized by sulfidizing an aromatic polyhalide compound, especially one composed mainly of a p-dihalobenzene such as p-dichlorobenzene or p-dibromobenzene, with a sulfur source selected from an alkali metal sulfide, a combination of hydrogen sulfide and an alkali metal base and a combination of sodium hydrosulfide and an alkali metal base. The preferred sulfur sources are a combination of sodium hydrosulfide and an alkali metal base. The preferred sulfur sources are a combination of sodium hydrosulfide and an alkali metal base. The preferred sulfur sources are a combination of sodium hydrosulfide and an alkali metal base. The alkali metal sulfide or alkali metal hydrosulfide may be used in the form of a hydrate.

In the present invention, organic solvents having an amide bond in the molecule, such as hexamethylphosphoramide, dimethylsulfoxide, dimethylacetamide, an N-alkyl-lactam and N,N-dialkylimidazolidinone, are used. Among them, N-alkyl-lactams are preferred, and N-methylpyrrolidone is especially preferred.

The above-mentioned sulfur source is mixed with the reaction solvent first. Before the condensation reaction, the mixture should be dehydrated so that the water content is lower than the predetermined level. The dehydration is ordinarily accomplished by distillation. The water content in the reaction mixture is controlled so that it is not higher than 5% by weight, preferably not higher than 1.0% by weight, based on the charged reaction components. The reason is that if the water content in the reaction mixture is too high, a polymer having a high molecular weight is difficult to obtain. In order to remove water from the reaction mixture effectively, it is preferable to carry out the reaction in a reaction or dehydration vessel equipped with a partial condenser having a rectifying effect.

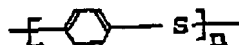
However, it has been found that the envisaged polymer having a reduced content of cyclic low-molecular-weight polymers cannot be obtained by only controlling the water content in the reaction mixture but the preparation of the envisaged polymer depends rather on the amount of the reaction solvent used, that is, the concentration of the reaction components. In general, a higher concentration of the reaction components is preferred. That is, a the amount of the solvent used is preferably small. However, if the amount of the solvent used is too small, uniform stirring becomes impossible and various disadvantages are brought about. In view of the ease of the above-mentioned dehydration and the controllability of the amount of the solvent used for the reaction, it is preferable to adopt a method in which the solvent is charged at the dehydrating step in an amount larger than the amount used for the reaction, and the excessive solvent is removed by distillation after termination of the dehydration while the amount of the distilled solvent is measured and controlled. The amount of the solvent used at the dehydrating step is not particularly critical, but in general, the solvent is used in an amount higher than about 400 g per mole of the aromatic polyhalide compound. However, after termination of the dehydration, that is, at the time of the reaction, the amount of the solvent is important. In general, the solvent is distilled off after termination of the dehydration

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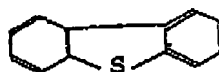
so that the amount of the solvent is adjusted to a level lower than 400 g, preferably 225 to 340 g, per mole of the aromatic polyhalide compound. Incidentally, since the concentration of the reaction components in the reaction mixture is maintained at a high level, in view of the ease of handling, the solvent should preferably be added after completion of the reaction to dilute the reaction mixture.

The aromatic polyhalide compound is added to the dehydrated reaction mixture to effect the polycondensation. The amount of the alkali metal sulfide used, or of the combination of hydrogen sulfide and alkali metal base or of the combination of alkali metal hydrosulfide and alkali metal base (calculated as the alkali metal sulfide) should preferably be 0.98 to 1.02 moles per mole of the aromatic polyhalide compound. The reaction temperature is in the range of from 200 to 280°C. The reaction is carried out under stirring for 1 to 10 hours. Since heat is generated in the initial stage, the reaction temperature may be changed stepwise. After termination of the reaction, the reaction mixture is cooled below 200°C, but if the temperature is excessively lowered, the reaction mixture becomes waxy and the discharge of the reaction product from the reaction vessel becomes impossible. Accordingly, a predetermined amount of the solvent should preferably be supplied to the reaction vessel to dilute the reaction mixture. It is preferred that the amount of the solvent added for dilution be such that the content of the solids (the total amount of the polymer formed and sodium chloride formed as a by-product) in the slurry is 20 to 35% by weight. It is necessary for the solvent used for dilution to be heated previously so as to prevent abrupt lowering of the temperature.

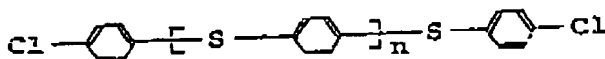
The diluted and slurried reaction mixture is subjected to hot solid-liquid separation by using a solid-liquid separator such as a filtering device or a centrifugal separator, and the mother liquid adhering to the separated solid is removed by washing with the heated solvent to obtain a solid substantially free of the adhering mother liquid. The temperature is important in these operations. It is necessary for the operations of solid-liquid separation and solvent-washing to be carried out at a temperature of at least 50°C but below the boiling point of the solvent, preferably from 100 to 190°C. The reason is that even if the amount of low-molecular-weight impurities can be reduced by reducing the amount of the solvent at the time of the reaction, it is impossible to reduce the impurity content to zero. Consequently, the formed low-molecular-weight impurities must be removed. The temperature dependency of the solubility of the impurities in the solvent is high, and a higher liquid temperature results in higher removal efficiency. However, if the liquid temperature is too high, the envisaged polymer is simultaneously separated, which is undesirable. In the present invention, it is important to separate and remove cyclic low-molecular-weight polymers. Examples of cyclic low-molecular-weight polymers formed as by-products, are cyclic low-molecular-weight compounds represented by the general formula



( $n = 2$  to 7, molecular weight = 216 to 756), inclusive of dibenzothiophene of the formula

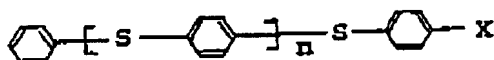


(molecular weight = 184). These compounds, especially dibenzothiophene, have a low molecular weight and have a boiling point of about 332°C. At the kneading step using an extruder or the injection molding step, these compounds are gasified generating an unpleasant smell and adversely affecting the physical properties. These low-molecular-weight compounds can be analyzed by gas chromatography using a thermal decomposition furnace at a furnace temperature of 300 to 330°C and a column temperature of 200 to 250°C. Moreover, these cyclic low-molecular-weight compounds inclusive of dibenzothiophene can be determined by the mass analysis (EI-MS) according to the electron impact ionization method. Furthermore, these low-molecular-weight compounds can be extracted and separated by using a solvent such as methylene chloride, chloroform or acetone. Non-cyclic low-molecular-weight polymers are formed as well as the above-mentioned cyclic low-molecular-weight compounds. Examples of such non-cyclic low-molecular-weight polymers are compounds of the general formula



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( $n = 0$  to 3, molecular weight = 225 to 579) and compounds represented by the general formula



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( $X = \text{H}$  or  $\text{Cl}$ ,  $n = 0$  to 3).

When the polyphenylene-sulfide resin containing the cyclic and non-cyclic low-molecular-weight polymers was heat-treated in an oxidative atmosphere to effect partial crosslinking and the resulting polyphenylenesulfide resin having a melt viscosity suitable for injection molding was examined, it was found that the cyclic low-molecular-weight polymers had remained in the resin, but the content of the non-cyclic low-molecular-weight polymers was drastically reduced and no substantial amounts of these polymers were detected. Accordingly even where the non-cyclic low-molecular-weight polymers are present, they will not cause trouble, if the resin is heat-treated in an oxidative atmosphere to form cross-links. Moreover, when the dependency of the mechanical strength of the resin upon the amount of the remaining cyclic low-molecular-weight polymers was examined, it was found that the mechanical strength can be highly improved by reducing the content of the cyclic low-molecular-weight polymers.

The cake obtained by the solid-liquid separation is directly placed into contact with water or hot water to dissolve sodium chloride formed as a by-product, or the adhering solvent is evaporated and the cake is then placed into contact with water or hot water to dissolve sodium chloride. The sodium chloride is then removed by filtration or centrifugal separation. If removal of sodium chloride by dissolution is performed under atmospheric pressure, the dissolution-filtration operation should be repeated several times. Under an elevated pressure, sodium chloride can be removed more efficiently. The polyphenylene sulfide, from which sodium chloride has been removed, can be dried by heating at 50 to 150°C under atmospheric or reduced pressure.

Since the melt viscosity of the so-obtained resin is low, the resin can be directly used only for a paint or as a special molding material. Accordingly, the resin is normally partially crosslinked in an oxidative atmosphere whereby the molecular weight of the polymer, that is, the melt viscosity of the polymer, is increased. Therefore, this partially crosslinked polymer is widely used for general purposes. In general, partial cross-linking can be accomplished by heat-treating the powdery polymer at a temperature of 200 to 270°C under circulation of air or by contacting the melt of the polymer with air at 280 to 350°C by using a device such as an extruder. If an oxidant such as hydrogen peroxide or chlorite is used, partial crosslinking can be accomplished at a relatively low temperature of 60 to 90°C. Preferably, the melt viscosity should be adjusted to 70 to 500 Pa·s, especially 150 to 400 Pa·s, as measured at 300°C by the partial crosslinking. Incidentally, the melt viscosity is measured under a load of 10 kgf by using a Koka type flow tester and a nozzle having a diameter of 0.5 mm and a length of 1.0 mm.

According to the process of the present invention, low-molecular-weight impurities formed as by-products in the preparation of the resin can be effectively removed and a polyphenylene-sulfide resin in which gas generation at the high-temperature kneading step is effectively controlled and which provides a molded article having highly improved mechanical strength especially impact strength, can be obtained.

The present invention will now be described in detail with reference to the following examples.

#### Example 1

A stainless steel autoclave equipped with a partial condenser and having a capacity of 1 liter was charged with 91 g (0.7 mole) of flaky sodium sulfide hydrate ( $\text{Na}_2\text{S}$  content = 60%) and 315 g of N-methylpyrrolidone, and dehydration was carried out under heating by circulating nitrogen gas. When the amount of aqueous N-methylpyrrolidone distilled at a temperature of 210°C reached 148 g, the mixture was cooled to 170°C. Then, 102.9 g (0.7 mole) of p-dichlorobenzene was added to the reaction mixture and reaction was carried out under a nitrogen gas pressure of  $2 \times 10^5$  Pa under stirring for 2 hours at 220°C and for 3 hours at 260°C. After termination of the reaction, the reaction mixture was cooled to 180°C, the inner pressure was gradually allowed to return to atmospheric pressure, and the reaction mixture was diluted with 110 g of N-methylpyrrolidone heated at 180°C. Then, the reaction mixture was subjected to reduced pressure filtration at 150°C by using a reduced pressure filter comprising a 325-mesh stainless steel net having a diameter of 10 cm. The filter cake was washed three times with 30 g of N-methylpyrrolidone maintained at 150°C, and then, the cake was washed five times with 300 g of hot water maintained at 80 to 90°C to

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remove sodium chloride. The water-washed polymer was dried under a reduced pressure at 150°C to obtain 72.5 g of a white powdery polymer. When the content of dibenzothiophene in about 10 mg of the powdery polymer was measured by gas chromatography using a thermal decomposition furnace, it was found that the content of dibenzothiophene was 660 ppm.

6 For comparison, the dibenzothiophene content in Ryton V-1 (commercially available polyphenylene-sulfide supplied by Phillips Petroleum Company, U.S.A.) was similarly measured. It was found that the dibenzothiophene content was 4,700 ppm.

10 A breaker was charged with 50 g of the obtained powdery polymer, and the polymer was heat-treated in a hot air drier maintained at 260°C while stirring the polymer now and then. When the heat treatment was conducted for 6 hours, the melt viscosity became 260 Pa s. At this point, the polymer was cooled and the treatment was stopped. The obtained powdery polymer and Ryton P-4 (supplied by Phillips Petroleum Company, U.S.A.) were analyzed. The obtained results are shown in Table I. Incidentally, when m/z of EI-MS of Ryton P-4 was determined, the detection sensitivity was reduced to 1/10.

Table 1

		Polymer of Example 1	Ryton P-4
		Brown powder	Brown powder
20	Appearance		
	Methylene chloride extraction ratio (%)	0.48	2.1
25	Dibenzothiophene content (ppm)	290	2,790
	m/z of EI-MS		
	184	+	++
30	216	+	+
	324	-	+
	432	+	+
35	540	++	+++
	648	+	++
40	Other m/z was not detected in substantial amounts		Other m/z was detected

45 As is apparent from the results shown in Table I, the content of cyclic low-molecular-weight impurities in the polyphenylene-sulfide resin obtained according to the process of the present invention is much lower than in the commercially available product.

#### Comparative Example I

50 A polyphenylene-sulfide resin was prepared from the same components as used in Example I in the same manner as described in Example I except that p-dichlorobenzene was added in the form of a solution in 130 g of N-methylpyrrolidone (NMP). After completion of the reaction, the reaction mixture was cooled to room temperature and 110 g of NMP was added to the mixture. The mixture was filtered at room temperature. Other procedures were the same as described in Example I. As a result, 73 g of a white powder was obtained.

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The dibenzothiophene content in this polymer was 2,300 ppm. When the polymer was heat-treated in the same manner as described in Example 1, quite a strong unpleasant smell was generated from the hot air drier. When the heat treatment was conducted for 10 hours, the melt viscosity became 320 Pa.s. At this point, the heat treatment was stopped. The methylene chloride extraction ratio of the obtained polymer was 2.6%.

#### Example 2

10 An autoclave having a capacity of 100 l, which was equipped with a jacket having an inner diameter of 80 mm and a length of 1,200 mm and a partial condenser filled with Raschig rings was charged with 9.1 kg (0.07 kg-mole) of flaky sodium sulfide hydrate ( $\text{Na}_2\text{S}$  content = 60%), and 0.18 kg of 48% aqueous sodium hydroxide and 21 kg of NMP were added. The temperature was elevated and dehydration was carried out under circulation of nitrogen gas. When the temperature of the reaction mixture became 210°C and the  
15 distilled amount of aqueous NMP reached 7.8 kg (3.6 kg of which was water), the dehydration was stopped and the mixture was cooled to 170°C. Then, 10.29 kg (0.07 kg-mole) of p-dichlorobenzene, 12.7 g (0.07 mole) of 1,2,4-trichlorobenzene and 3.5 kg of NMP were added to the mixture, and reaction was carried out under a nitrogen gas pressure of  $3.0 \times 10^5$  Pa at 220°C for 2 hours and at 260°C for 3 hours. Then, the reaction mixture was cooled to 180°C. The remaining pressure was released and 43.5 kg of NMP heated at  
20 150°C was added to the reaction mixture for dilution. Then, the diluted mixture was transferred to a compression filter comprising a net having a mesh size of 25  $\mu\text{m}$  and a filtration area of 0.2  $\text{m}^2$ . Compression filtration was carried out at a temperature maintained at 150°C by using nitrogen gas. The adhering mother liquid was removed from the obtained cake by spraying twice 6 kg of NMP maintained at 150°C. Then, the wet cake was dried at 150°C under a reduced pressure of 4000 Pa (30 Torr). Solid was  
25 washed three times with 45 kg of city water maintained at 80°C and twice with deionized water to remove sodium chloride. The solids were dried at 80°C under a reduced pressure of 30 Torr to obtain a grayish white powdery polymer. The yield was 96.2%. The polymer was heat-treated at 240°C in an oven while being stirred, and when the melt viscosity reached 250 Pa.s, the polymer was cooled. In order to obtain a  
30 sample to be used for the measurement of the mechanical strength, the polymer was extruded in the form of a strand at a temperature of 300 to 320°C by using an extruder, and the strand was chipped. Molding was carried out at a mold temperature of 120°C by using an injection molding machine, and the physical properties of the molded article were determined. The results obtained are shown in Table 2.

#### 35 Examples 3 through 5 and Comparative Examples 2 and 3

Polyphenylene-sulfide resins were prepared in the same manner as described in Example 2 except that the conditions were those shown in Table 2. The results obtained are shown in Table 2.

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Table 2

	Example 2	Example 3	Example 4	Example 5	Comparative Example 2	Comparative Example 3
(1) Amount (g/mole) of NMP used at reaction	290	290	250	220	400	450
(2) Filtration temperature (°C)	150	100	80	160	30	30
(3) Yield (%) of polymer	96.2	96.4	97.2	96.0	96.0	97.0
(4) Smell at operation in extruder	Slight	Slight	Slight	Slight	Extrema	Extrema
(5) Melt viscosity (Pa·s at 300°C) after heat treatment	250	220	280	260	230	250
(6) Methylene chloride extraction ratio (%)	0.8	1.2	1.3	0.7	2.1	2.3
(7) Dibenzothioophene content (ppm)	405	530	540	320	2,950	3,400
(8) Mechanical strength characteristics of non-reinforced polymer						
Flexural strength (kg/cm <sup>2</sup> )	1,270	1,120	1,150	1,320	944	795
Flexural modulus (kg/cm <sup>2</sup> )	35 x 10 <sup>3</sup>	35 x 10 <sup>3</sup>	35 x 10 <sup>3</sup>	35 x 10 <sup>3</sup>	34 x 10 <sup>3</sup>	34 x 10 <sup>3</sup>
Tensile strength (kg/cm <sup>2</sup> )	523	510	512	680	420	418
180° Impact strength (kg·cm/cm <sup>2</sup> )	1.4	1.4	1.3	1.8	1.2	1.1
notched	12.9	11.9	11.1	13.8	5.1	4.9
unnotched						



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## Claims

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1. A process for the preparation of polyphenylene-sulfide resins, which comprises reacting an aromatic polyhalide compound with an alkali metal sulfide, or hydrogen sulfide and an alkali metal base, or an alkali metal hydrosulfide and an alkali metal base in the presence of an amide polar solvent to form a polyphenylene-sulfide resin, characterized in that (a) the reaction is carried out in the absence of a polymerization aid, (b) the amide polar solvent is used in an amount not larger than 400 g per mole of the aromatic polyhalide compound, and (c) the polymerization liquid obtained by completion of the reaction is subjected to hot solid-liquid separation at a temperature of at least 50°C but below the boiling point of the solvent used, and the separated solids are washed with the solvent used for the reaction, which is heated to a temperature at least 50°C but below its boiling point, to remove the mother liquid adhering to the solids, whereby a polyphenylene-sulfide resin is obtained which has a cyclic oligomer content lower than 1.5% by weight, as determined according to the methylene chloride extraction method.

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2. The process according to claim 1 wherein the polyphenylene-sulfide resin prepared has at least 90% by mole of recurring units represented by the formula

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3. The process according to claim 1 wherein the amide polar solvent is hexamethylphosphoramide, dimethylsulfoxide, dimethylacetamide, an N-alkyl-lactam or N,N-dialkylimidazolidinone.

4. The process according to claim 1 wherein the amount of the amide polar solvent is from 225 to 340 g per mole of the aromatic polyhalide compound.

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5. The process according to claim 1 wherein the amount of the alkali metal sulfide, of the combination of hydrogen sulfide and alkali metal base or of the combination of alkali metal hydrosulfide and alkali metal base calculated as the alkali metal sulfide is 0.98 to 1.02 moles per mole of the aromatic polyhalide compound.

6. The process according to claim 1 wherein the reaction is carried out at a temperature of 200 to 280°C for 1 to 10 hours.

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7. The process according to claim 1 wherein the polymerization liquid obtained by completion of the reaction is diluted with the amide polar solvent to such an extent that the solids content in the diluted liquid is 20 to 35% by weight, and then subjected to the hot solid-liquid separation.

8. The process according to claim 1 wherein the solid-liquid separation and the solvent-washing are carried out at a temperature of 100°C to 190°C.

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